Synthesis and Electroluminescent Properties of New Amorphous Cyclohexyl- and Hexyl-substituted Ter(9,9-dialkylfluorene)s

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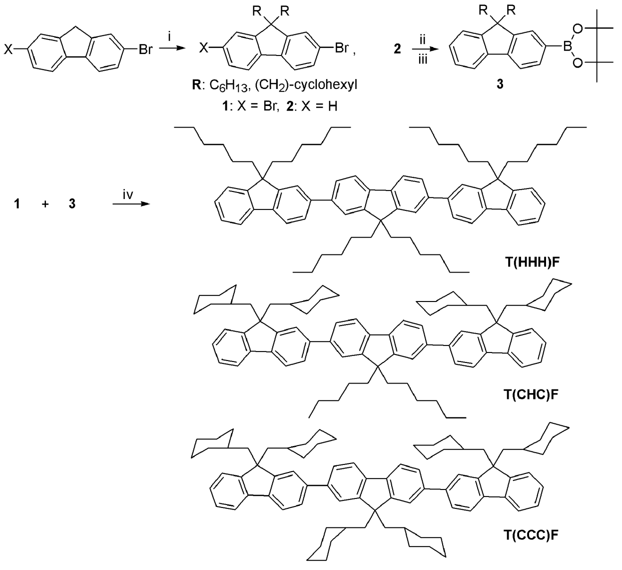
A series of ter(9,9-dialkylfluorene)s (TFs) containing cyclohexyl and hexyl side groups has been synthesized via the Suzuki coupling reaction. Their chemical structures were characterized by ^{1}H NMR and ^{13}C NMR. All TFs were soluble in common organic solvents and showed good thermal stability up to 400 °C. In particular, T(CHC)F composed of two 9,9-bis(cyclohexylmethyl)fluorenes and one dihexylfluorene showed improved thermal stability over T(HHH)F and was found to be amorphous, unlikely with T(CCC)F. A light-emitting diode device fabricated with an ITO/2-TNATA/NPB/TFs/Alq_3/Liq/Al configuration exhibited blue light emission with EL maxima at 450 nm and EL efficiency of 1.1 cd/A.

Fluorene-based oligomers and polymers are generally regarded as the most promising candidates for blue organic light-emitting diodes (OLEDs). Oligomers have advantages over polymers in terms of purity and structure uniformity.[1] Fluorene trimers are known to be long enough to emit blue light. However, oligomers are limited by a tendency toward crystallization and a low glass-transition temperature, in comparison to polymers. Since crystallization tends to create grain boundaries that limit charge transport and cause poor contact, it is desirable to create thermally and morphologically stable amorphous molecular materials that do not tend to be crystallized on heating above glass-transition temperature (T_g) for practical applications. In this manner, glass-forming conjugated oligomers with improved thermal stability have been synthesized, which includes starburst molecules and spiro-linked oligo(*p*-phenylene)s and oligo(triphenylamine)s.[2–5] In particular, spiro-linked terfluorenes have attracted much attention for use as blue-emitting materials for OLEDs, which form stable nonpolymeric organic glasses with high glass-transition temperatures.[6–9] Here, we report on the synthesis and thermal and optical properties of cyclohexyl- and/or hexyl-substituted terfluorenes as new amorphous materials emitting blue light. We outline our strategy for improving the material properties of terfluorenes. The thermal stability and the phase-transition behavior were varied with the incorporated side groups of terfluorenes.

New ter(9,9-dialkylfluorene)s (TFs), T(HHH)F, T(CHC)F, and T(CCC)F, were synthesized by using the Suzuki coupling reaction.[10] The synthetic procedures of TFs are outlined in Scheme 1. Their chemical structures were verified by ^{1}H NMR and ^{13}C NMR. The resulting oligomers were well soluble in common organic solvents due to the introduced side groups. The thermal stabilities of the TFs were evaluated under nitrogen atmosphere by thermogravimetric analysis (TGA). All TFs showed good thermal stability, as weight loss was less than 5% on heating to about 400 °C. The phase transition temperatures (i.e., T_g), investigated with differential scanning calorimetry (DSC) in nitrogen, were dramatically increased by increasing the number of cyclohexyl-substituted fluorene units (See Table 1; T(HHH)F < T(CHC)F < T(CCC)F). Upon heating beyond T_g, T(CCC)F composed of three-cyclohexyl-substituted fluorenes was found to crystallize at 210 °C, referred to as the crystallization temperature, T_k. This is an indication of morphological instability, as commonly encountered with nonpolymeric organic materials. Further heating revealed the crystalline melting point,



Scheme 1. Synthetic procedure of TFs: (i) 1-bromooctane, tetra(*n*-butyl)ammonium bromide, NaOH (aq, 50 wt %), toluene, reflux; (ii) *n*-BuLi, THF, −78 °C for 2 h; (iii) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, −78 °C for 1 h, then room temperature overnight; (iv) $Pd(PPh_3)_4$, toluene, ethanol, Na_2CO_3 (aq, 2 M), reflux.

Table 1. Thermal properties of terfluorenes

	T_g[a]/°C	T_k[a]/°C	T_m[a]/°C	$T_{5\%}$[b]/°C
T(HHH)F	30	—[c]	—[c]	380
T(CHC)F	70	—[c]	—[c]	390
T(CCC)F	100	210	255	400

[a] T_g: glass-transition temperature, T_k: crystallization temperature, T_m: melting temperature. [b] Temperature resulting in 5% weight loss based on the initial weight. [c] Not detected.

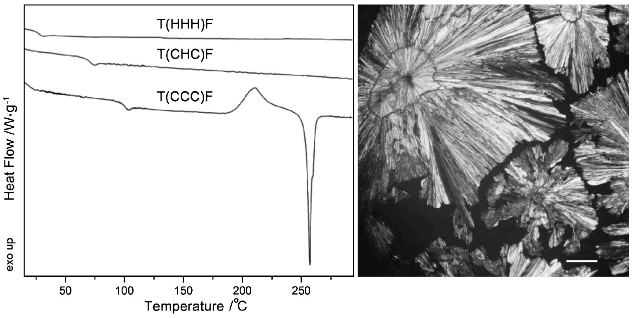


Figure 1. DSC thermograms of TFs and optical microscopy image of T(CCC)F at 200 °C. Scale bar represents 200 µm.

T_m, at 255 °C. An optical microscopy image of T(CCC)F film measured at 200 °C is also shown in Figure 1. In contrast, T(HHH)F and T(CHC)F were morphologically stable upon heating beyond their T_g's.

Three TFs showed similar optical properties. The UV–vis absorption maxima of TFs appeared at 350 nm. The PL emission spectra of the TFs in the chloroform solution showed typical vibronically structured bands comprising a maximum, a shoulder and a tail, which appeared at 393, 414, and 440 nm respectively. As films, the emission maxima of TFs were red-shifted (399 nm) compared to those of the solution state. The normalized UV–vis absorption and PL emission spectra of the T(CHC)F film are shown in Figure 2a. In addition, the ionization potential I_p and electron affinity E_a of the terfluorenes are −5.85 and −2.65 eV respectively, as determined by cyclic voltammetry (CV).

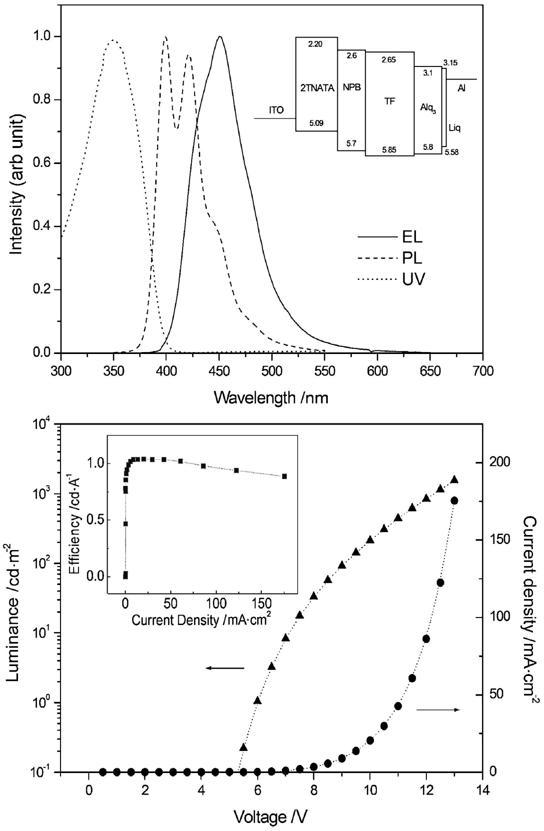


Figure 2. (a) UV–vis, PL, and EL spectra of T(CHC)F films. Inset: An energy diagram of the device (in eV). (b) Luminance vs. voltage and current density vs. voltage plots. Inset: Luminous efficiency vs. current density.

In order to investigate the electroluminescence properties and the current–voltage–luminance characteristics of the synthesized oligomers, devices with the configuration ITO/2-TNATA (60 nm)/NPB (40 nm)/TFs (35 nm)/Alq_3 (20 nm)/Liq (3 nm)/Al were fabricated. 4,4,4-Tris[*N*-(2-naphthyl)phenylamino]triphenylamine (2-TNATA), *N*,*N*′-di(l-naphthyl)-*N*,*N*′-diphenyl-1,1′-biphenyl-4,4′-diamine (NPB) and tris(8-hydroxyquinolinato)aluminum (Alq_3) were used as hole-injecting, hole-transport, and electron-transport materials, respectively.[11] The 8-hydroxyquinolinatolithium (Liq) was used as an electron-injection layer, which showed better performance tolerance to the injection layer thickness than lithium fluoride (LiF).[12,13] TF compounds were used as blue emitters. Three TFs showed similar EL characteristics. As an example, the EL spectra and the current–voltage–luminance (*I*–*V*–*L*) characteristics of the device using T(CHC)F are shown in Figure 2. All TFs emitted light of a blue color with a maximum emission at 450 nm and a full width at half maximum (fwhm) of only 60 nm. This emission has the CIE coordinates (0.15 and 0.09), which are very close to the standard for blue used by the National Television System Committee (NTSC) (0.15 and 0.08) and are superior to the previously reported oligofluorene derivatives. The maximum EL efficiency was found to be 1.1 cd/A and up to about 200 mA/cm^2 the efficiency is maintained near 1.0 cd/A.

In summary, a series of cyclohexyl- and hexyl-substituted ter(9,9-dialkylfluorene)s have been synthesized. Among them, T(CHC)F is found to be amorphous and shows improved thermal stability. New TFs can be used as emitting materials for producing stable blue emission for full-color organic EL devices.

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